



In re Application of: :  
A. Nakajima et al. : Art unit: 1755  
Serial No. 10/647,169 :  
Filed: August 21, 2003 :  
For: INK-JET IMAGE FORMING :  
METHOD :  
x

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I, Fumio ISHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 252357/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

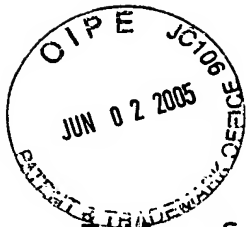
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Fumio ISHII

Dated: This 9th day of May, 2005.



**Patent Application No. 252357/2002**

**Title of the Document:** APPLICATION FOR PATENT

**Reference Number:** DKT2482743

**Address:** The Director General of the  
Patent Office

**International  
Patent Classification:** B41J 2/01  
B41M 5/00

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**Representative:** Fumio IWAI

**Indication of Fee:**

**Prepayment Registration  
Number:** 012265

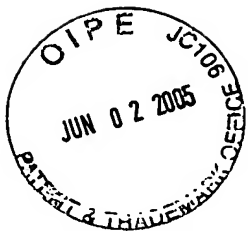
**Amount of Payment** 21000

**List of Documents Attached:**

<b>Title of Document:</b>	Specification	1
<b>Title of Document:</b>	Drawings	1
<b>Title of Document:</b>	Abstract	1

**Necessity of Proof**

**Required**



[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

INK-JET IMAGE FORMING METHOD

[WHAT IS CLAIMED IS:]

Claim 1. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein an energy input amount to an exposure light source, which is employed for said light exposure, is 0.1 - 50 W/cm and said photocurable ink comprises a compound having an oxetane ring in which at least position 2 is substituted.

Claim 2. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein the time to initiate exposure, after said photocurable ink ejected from said ink-jet head impinges on a substrate, is in the range of 0.001 - 2 seconds and said photocurable ink comprises a compound having an oxetane ring in which at least position 2 is substituted.

Claim 3. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an

ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein said photocurable ink comprises a compound having an oxetane ring in which at least position 2 is substituted, and illuminance on the surface of said substrate during said light exposure after said photocurable ink is ejected is adjusted to be in the range of 0.1 - 50 mW/cm<sup>2</sup> at 200 - 450 nm.

Claim 4. The ink-jet image forming method, described in any one of claims 1 to 3, wherein light which is used for said light irradiation or said light exposure is ultraviolet radiation, and the peak wavelength of said ultraviolet radiation is in the range of 200 - 430 nm.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[TECHNICAL FIELD PERTAINING THE INVENTION]

The present invention relates to an ink-jet image forming method.

[0002]

[PRIOR ART]

Since a photocurable type (also called actinic radiation curable type) ink-jet image forming method makes it possible to carry out printing onto various substrates

without providing a special image receiving layer, heretofore techniques for this have received attention mainly for business use as well as for industrial use. For example, in ultraviolet radiation curable ink-jet image formation, a method is customarily employed in which active species are generated in a short time generally employing high power light sources such as a high pressure mercury lamp or a metal halide lamp, resulting in curing.

[0003]

However, when the aforesaid method is applied to a radical polymerization system, polymerization is inhibited by oxygen, and the aforesaid method is unsuitable for curing minute ink droplets formed during ink-jet printing. As a result, it has been proposed to use a cation polymerization based ink.

[0004]

Further, preferably employed as monomers used in ink-jet ink are those which are capable of easily controlling the shape of dots and of producing fine and accurate images. For example, Japanese Patent Publication Open to Public Inspection No. 2000-181386 discloses preferred embodiments in which high speed monomers are employed.

[0005]

However, when the high power light source, disclosed in the aforesaid patent, is employed, problems are pointed out in which the characteristics of cured layers tend to degrade and the use of the aforesaid high power light sources is not preferred from the viewpoint of electric power saving of the printer.

[0006]

[PROBLEMS THEM PRESENT INVENTION INTENDS TO SOLVE]

A first objective of the present invention is to provide an ink-jet image forming method which exhibits a high speed, high scratch resistance of the ink surface and excellent adhesion property. A second objective is to provide an ink-jet image forming method which minimizes staining onto a head with sublimated materials formed by curing, minimizes nozzle clogging due to entrance of stray light and further effectively minimizes degradation of image quality due to fluctuation of dot shape due to variation of the substrate.

[0007]

[MEANS TO SOLVE THE PROBLEMS]

The aforesaid objectives of the present invention were achieved employing embodiments 1 - 4, described below.

[0008]



1. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein an energy input amount to an exposure light source, which is employed for said light exposure, is 0.1 - 50 W/cm and said photocurable ink comprises a compound having an oxetane ring in which at least position 2 is substituted.

[0009]

2. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein the time to initiate exposure, after said photocurable ink ejected from said ink-jet head impinges on a substrate, is in the range of 0.001 - 2 seconds and said photocurable ink comprises a compound having an oxetane ring in which at least position 2 is substituted.

[0010]

3. In an ink-jet image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method wherein said photocurable ink

comprises a compound having an oxetane ring in which at least position 2 is substituted, and illuminance on the surface of said substrate during said light exposure after said photocurable ink is ejected is adjusted to be in the range of 0.1 - 50 mW/cm<sup>2</sup> at 200 - 450 nm.

[0011]

4. The ink-jet image forming method, described in any one of 1. - 3. above, wherein light which is used for said light irradiation or said light exposure is ultraviolet radiation, and the peak wavelength of said ultraviolet radiation is in the range of 200 - 430 nm.

[0012]

The present invention will now be detailed.

<<Photocurable Ink (also called Actinic Radiation Curable Ink)>>

Description of the photocurable ink according to the image forming method of the present invention follows.

[0013]

In order to achieve the effects described in the present invention, i.e., to form ink-jet images which result in a high speed, and exhibit high scratch resistance of the ink surface and excellent adhesion property, it is an essential condition that oxetane compounds in which at least

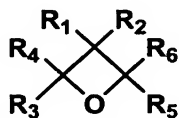
position 2 is substituted is used in the photocurable ink. Preferably employed as the aforesaid oxetane compounds are compounds having in the molecule at least one oxetane ring represented by General Formula (1) described below.

[0014]

<<Compounds having an oxetane ring in which position 2 is substituted>>

[0015]

General Formula (1)



[0016]

wherein,  $R_1 - R_6$  each represents a hydrogen atom or a substituent, however, at least one of the groups represented by  $R_3 - R_6$  is a substituent.

[0017]

In General Formula (1), examples of substituents represented by each of  $R_1 - R_6$  include a fluorine atom, an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, or a butyl group), a fluoroalkyl group having 1 - 6 carbon atoms, an allyl group, an aryl group (e.g., a phenyl group or a naphthyl group), a

furyl group, or a thienyl group. Further, these groups may have an additional substituent.

[0018]

<<Compounds having one oxetane ring in the molecule>>

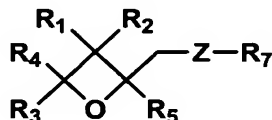
Further, of the compounds represented by aforesaid General Formula (1), preferably employed are compounds having the oxetane ring represented by General Formulas (2) - (5) described below.

[0019]

General Formula (2)



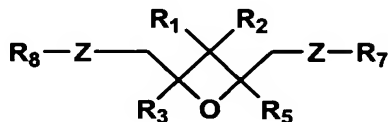
General Formula (3)



General Formula (4)



General Formula (5)



[0020]

wherein,  $R_1 - R_6$  each represents a hydrogen atom or a substituent,  $R_7$  and  $R_8$  each represents a substituent, and  $Z$  represents an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

[0021]

In General Formulas (2) - (5),  $R_1 - R_6$  each represents the same substituent as that represented by each of  $R_1 - R_6$  in aforesaid General Formula (1).

[0022]

In General Formulas (2) - (5), substituents represented by each of  $R_7$  and  $R_8$  include an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, or a propyl group), an alkenyl group having 1 - 6 carbon atoms (e.g., a 1-propenyl group, a 2-propenyl group, a 2-methyl-1-propenyl group, a 2-methyl-2-propenyl group, a 1-butenyl group, a 2-butenyl group, or a 3-butenyl group), an aryl group (e.g., a phenyl group or a naphthyl group), an aralkyl group (e.g., a benzyl group, a fluorobenzyl group, or a methoxybenzyl group), an acyl group having 1 - 6 carbon atoms (e.g., a propylcarbonyl group, a butylcarbonyl group, or a pentylcarbonyl group), an alkoxycarbonyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbonyl group, a

propoxycarbonyl group, or a butoxycarbonyl group), an alkylcarbamoyl group having 1 - 6 carbon atoms (e.g., a propylcarbamoyl group or a butylpentylcarbamoyl group), and an alkoxycarbamoyl group (e.g., an ethoxycarbamoyl group).

[0023]

In General Formulas (2) - (5), listed as an oxygen atom or a sulfur atom, or divalent hydrocarbon groups which may have an oxygen atom or a sulfur atom in the main chain, are an alkylene group (e.g., an ethylene group, a trimethylene group, a tetramethylene group, a propylene group, an ethylethylene group, a pentamethylene group, a hexamethylene group, a heptamethylene group, an octamethylene group, nonamethylene group, or a decamethylene group), an alkenylene group (e.g., a vinylene group or a propenylene group), and an alkynylene group (e.g., an ethynylene group or a 3-pentynylene group). Further, the carbon atom of the aforesaid alkylene group, alkenylene group, and alkynylene group may be replaced with an oxygen atom or a sulfur atom.

[0024]

Of the aforesaid substituents,  $R_1$  is preferably a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group). Specifically, the ethyl group of these is preferably employed. Further, either  $R_7$  or  $R_8$  is preferably a

propyl group, a butyl group, a phenyl group, or a benzyl group, while Z is preferably a hydrocarbon group (e.g., an alkylene group, an alkenylene group, or an alkynylene group) having neither an oxygen atom nor a sulfur atom.

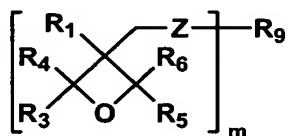
[0025]

<<Compounds having at least two oxetane rings in the molecule>>

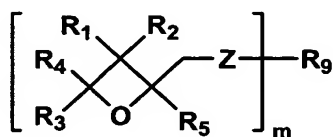
Further, in the present invention, it is possible to employ compounds having at least two oxetane rings in the molecule, which are represented by General Formulas (6) and (7) described below.

[0026]

General Formula (6)



General Formula (7)



[0027]

wherein Z is the same as the groups used in aforesaid General Formulas (2) - (5); m represents 2, 3, or 4; R<sub>1</sub> - R<sub>6</sub> each represents a hydrogen atom, a fluorine atom, an alkyl

group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, or a butyl group), a fluoroalkyl group having 1 - 6 carbon atoms, an allyl group, an aryl group (e.g., a phenyl group or a naphthyl group), or a furyl group.; however, in General Formula (6), at least one of  $R_2 - R_6$  is to be a substituent;

[0028]

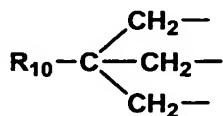
wherein  $R_9$  represents a straight or branched alkylene group having 1 - 12 carbon atoms, a straight or branched poly(alkyleneoxy) group or a divalent group selected from the group consisting of General Formulas (9), (10), and (11) described below.

[0029]

Preferably employed as the aforesaid branched alkylene group having 1 - 12 carbon atoms are alkylene groups represented by General Formula (8) described below.

[0030]

General Formula (8)



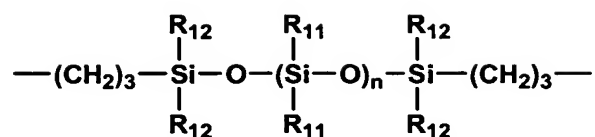
[0031]

wherein  $R_{10}$  represents a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group).



[0032]

General Formula (9)

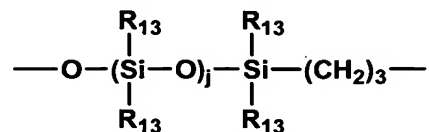


[0033]

wherein n represents 0 or an integer of 1 - 2,000, R<sub>12</sub> represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group), and R<sub>11</sub> represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group), or the group represented by General Formula (12) described below.

[0034]

General Formula (12)



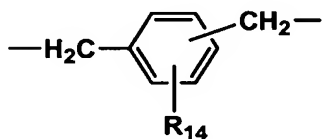
[0035]

wherein j represents 0 or an integer of 1 - 100, and R<sub>13</sub> represents an alkyl group having 1 - 10 carbon atoms

(e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group).

[0036]

General Formula (10)

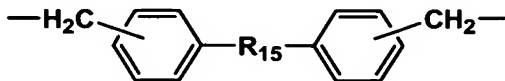


[0037]

wherein  $R_{14}$  represents a hydrogen atom or an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group), a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), a nitro group, a cyano group, a mercapto group, an alkoxycarbonyl group (e.g., a methyloxycarbonyl group, an ethyloxycarbonyl group, or a butyloxycarbonyl group), or a carboxyl group.

[0038]

General Formula (11)



[0039]

wherein  $R_{15}$  represents an oxygen atom, a sulfur atom, -NH-, -SO-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, -C(CH<sub>3</sub>)<sub>2</sub>-, or -C(CF<sub>3</sub>)<sub>2</sub>-.

[0040]

Embodiments of the preferred partial structure of compounds having an oxetane ring employed in the present invention are as follows. For example, in aforesaid General Formulas (6) and (7),  $R_1$  is preferably a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group), and is more preferably an ethyl group. Further, preferably employed as  $R_9$  is a hexamethylene group or a group in which  $R_{14}$  is a hydrogen atom in aforesaid General Formula (10).

[0041]

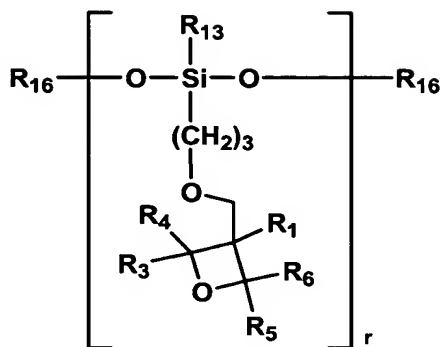
In aforesaid General Formula (8), it is preferable that  $R_{10}$  is an ethyl group,  $R_{12}$  and  $R_{13}$  each is a methyl group, and Z is a hydrocarbon group which contains neither an oxygen atom nor a sulfur atom.

[0042]

Further, listed as one example of preferred embodiments of compounds having an oxetane ring according to the present invention is the compound represented by General Formula (13) described below.

[0043]

General Formula (13)



[0044]

wherein  $r$  represents an integer of 25 - 200;  $R_{16}$  represents an alkyl group having 1 - 4 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, or a butyl group), or a trialkylsilyl group;  $R_1$ ,  $R_3$ ,  $R_5$ , and  $R_6$  each is the same as a substituent represented by each of  $R_1 - R_6$  in aforesaid General Formula (1), however, at least one of  $R_3 - R_6$  is a substituent.

[0045]

Specific examples of compounds having an oxetane ring, in which position 2 is substituted, are shown as Exemplified Compounds 1 - 13. However, the present invention is not limited thereto.

[0046]

1: trans-3-tert-butyl-2-phenyloxetane

- 2: 3,3,4,4-tetramethyl-2,2-diphenyloxetane
- 3: di[3-ethyl(2-methoxy-3-oxetanyl)]methyl ether
- 4: 1,4-bis(2,3,4,4-tetramethyl-3-ethyl-oxetanyl)butane
- 5: 1,4-bis(3-methyl-3-ethyloxetanyl)butane
- 6: di(3,4,4-trimethyl-3-ethyloxetanyl)methyl ether
- 7: 3-(2-ethyl-hexyloxymethyl)-2,2,3,4-tetramethyloxetane
- 8: 2-(2-ethyl-hexyloxy)-2,3,3,4,4-pentamethyl-oxetane
- 9: 4,4'-bis[(2,4-dimethyl-3-ethyl-3-oxetanyl)methoxy]biphenyl
- 10: 1,7-bis(2,3,3,4,4-pentamethyl-oxetanyl)heptane
- 11: oxetanyl silsesquioxatane
- 12: 2-methoxy-3,3-dimethyloxane
- 13: 2,2,3,3-tetramethyloxetane

It is possible to synthesize the compounds according to the present invention, which have an oxetane ring in which at least position 2 is substituted, with reference to publications described below.

[0047]

- (1) Hu Xianming, Richard M. Kellogg, Synthesis, 533 - 538, May (1995)
- (2) A. O. Fitton, J. Hill, D. Ejane, R. Miller, Synth., 12, 1140 (1987)
- (3) Toshiro Imai and Shinya Nishida, Can. J. Chem. Vol. 59, 2503 - 2509 (1981)

- (4) Nobujiro Shimizu, Shintaro Yamaoka, and Yuho Tsuno, Bull. Chem. Soc. Jpn., 56, 3853 - 3854 (1983)
  - (5) Walter Fisher and Cyril A. Grob, Helv. Chim. Acta., 61, 2336 (1987)
  - (6) Chem. Ber. 101, 1850 (1968)
  - (7) "Heterocyclic Compounds with Three- and Four-membered Rings", Part Two, Chapter IX, Interscience Publishers, John Wiley & Sons, New York (1964)
  - (8) Bull. Chem. Soc. Jpn., 61, 1653 (1988)
  - (9) Pure Appl. Chem., A29 (10), 915 (1992)
  - (10) Pure Appl. Chem., A30 (2 & amp;3), 189 (1993)
  - (11) Japanese Patent Application Open to Public Inspection No. 6-16804
  - (12) DE 10221858
- (Content in Photocurable Ink)

The amount of compounds according to the present invention, which have an oxetane ring in which at least position 2 is substituted, in a photocurable ink is preferably 1 - 97 percent by weight, and is more preferably 30 - 95 percent by weight.

[0048]

(Use of oxetane compounds in combination with other monomers)

Further, compounds according to the present invention, which have oxetane ring(s) in which at least position 2 is substituted, may be employed individually or in combinations with two types which have different structures. Further, the aforesaid compound may be employed in combination with photopolymerizable compounds such as photopolymerizable monomers or polymerizable monomers described below. When employed in combinations, it is preferable that a mixture is prepared so that the amount of compounds having oxetane ring(s) in the aforesaid mixture is adjusted to 10 - 98 percent by weight. Still further, it is preferable that the amount of other photopolymerizable compounds such as photopolymerizable monomers and polymerizable monomers is adjusted to 2 - 90 percent by weight.

[0049]

<<Photopolymerizable Compounds>>

Photopolymerizable compounds used in the present invention, especially photopolymerizable cationic monomers, will now be described.

[0050]

Employed as photopolymerizable cationic monomers may be various types of cationic polymerizable monomers known in the art. Listed, for example, are epoxy compounds, vinyl ether

compounds, and oxetane compounds exemplified in Japanese Patent Application Open to Public Inspection Nos. 6-9714, 2001-31892, 2001-40068, 2001-55507, 2001-310938, 2001-310937, and 2001-220526.

[0051]

Listed as epoxy compounds are aromatic epoxides, alicyclic epoxides, and aliphatic epoxides.

[0052]

Preferred aromatic epoxides include di- or polyglycidyl ethers which are prepared by allowing polyhydric phenol having at least one aromatic nucleus or alkylene oxide addition products thereof to react with epichlorohydrin. Examples include di- or polyglycidyl ethers of bisphenol A or alkylene oxide addition products thereof, di- or polyglycidyl ethers of hydrogenated bisphenol A or alkylene oxide addition products thereof, and novolak type epoxy resins. Herein, listed as alkylene oxides are ethylene oxide and propylene oxide.

[0053]

Preferred as alicyclic epoxides are compounds comprising cyclohexane oxide or cyclopentane oxide, which are prepared by epoxyfying compounds having at least one cycloalkane ring such as a cyclohexane or cyclopentane ring,



employing suitable oxidizing agents such as hydrogen peroxide or peracids.

[0054]

Preferred aliphatic epoxides include di- or polyglycidyl ethers of aliphatic polyhydric alcohols or alkylene oxide addition products thereof. Representative examples include diglycidyl ethers of alkylene glycol such as diglycidyl ether of ethylene glycol, diglycidyl ether of propylene glycol, or diglycidyl ether of 6-hexanediol; polyglycidyl ethers of polyhydric alcohol such as di- or triglycidyl ethers of glycerin or alkylene oxide addition products thereof; and diglycidyl ethers of polyalkylene glycol such as diglycidyl ethers of polypropylene glycol or alkylene oxide addition products thereof. Herein, listed as alkylene oxides are ethylene oxide and propylene oxide.

[0055]

Of these epoxides, from the viewpoint of quick curability, preferred are aromatic epoxides and alicyclic epoxides and particularly preferred are alicyclic epoxides. In the present invention, the aforesaid epoxides may be employed individually or in proper combinations of at least two types.

[0056]

<<Vinyl Ether Compounds>>

Vinyl ether compounds employed in the present invention will now be described.

[0057]

Examples of vinyl ether compounds include di- or trivinyl ether compounds such as ethylene glycol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, propylene glycol divinyl ether, dipropylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, cyclohexanedimethanol divinyl ether, and trimethylolpropane trivinyl ether, and monovinyl ether compounds such as ethyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxybutyl vinyl ether, 2-ethylhexyl vinyl ether, cyclohexanedimethanol monovinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, isopropenyl ether-O-propylene carbonate, dodecyl vinyl ether, diethylene glycol monovinyl ether, and octadecyl vinyl ether.

[0058]

Of these vinyl ether compounds, when taking into account curability, adhesion properties, and surface hardness, di- or trivinyl ether compounds are preferred, and

divinyl ether compounds are particularly preferred. In the present invention, the aforesaid vinyl ether compounds may be employed individually or in combinations of at least two types.

[0059]

<<Oxetane Compounds>>

In the present invention, other than compounds having oxetane ring(s), according to the present invention, in which at least position 2 is substituted, oxetane compounds may be used together with the aforesaid compounds. It is possible to use any of the oxetane compounds, known in the art, such as those described, for example, in Japanese Patent Application Open to Public Inspection Nos. 2001-220526 and 2001-310937.

[0060]

<<Photopolymerization Initiators>>

Photopolymerization initiators employed in the present invention will now be described.

[0061]

In the present invention, in order to efficiently carry out the curing reaction of a photocurable ink, it is preferable that curing is carried out in the presence of photopolymerization initiators known in the art. The

aforesaid photopolymerization initiators are divided mainly into two types, i.e., an intramolecular bond cleavage type and an intramolecular hydrogen extraction type.

[0062]

Examples of intramolecular bond cleavage type photopolymerization initiators include acetophenone based compounds such as diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropane-1-one, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-one, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, 1-hydroxycyclohexyl-phenyl ketone, 2-methyl-2-morpholino(4-thiomethylphenyl)propane-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane; benzoin such as benzoin, benzoin methyl ether, and benzoin isopropyl ether; acylphosphine oxide based compounds such as 2,4,6-trimethylbenzoindiphenylphosphine oxide; and benzyl and methylphenylglyoxy ester.

[0063]

On the other hand, examples of intramolecular hydrogen extraction type photopolymerization initiators include benzophenone based compounds such as benzophenone, o-benzoylbenzoic acid methyl-4-phenylbenzophenone, 4,4'-dichlorobenzophenone, hydroxybenzophenone, 4-benzoyl-4'-

methyl-diphenyl sulfide, acrylated benzophenone, 3,3',4,4'-terta(t-butylperoxycarbonyl)benzophenone, and 3,3'-dimethyl-4-methoxybenzophenone; thioxanthone based compounds such as 2-isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, and 2,4-dichloroxanthone; aminobenzophenone based compounds such as Michler's ketone and 4,4'-diethylaminobenzophenone; and 10-butyl-2-chloroacrydone, 2-ethylanthraquinone, 9,10-phenanthlenequinone, and camphorquinone.

[0064]

The blending amount of photopolymerization initiators is preferably in the range of 0.01 - 10.00 percent by weight in the photocurable ink composition (also called the actinic light curable composition).

[0065]

<<Recording Media>>

Recording media employed in the present invention will be described.

[0066]

Recording media employed in the present invention are comprised of metals such as aluminum, iron, or copper, plastics such as vinyl chloride, acryl, polycarbonate, polyethylene terephthalate, acrylonitrile-butadiene-styrene

copolymers, polyethylene, or polypropylene, ceramics such as glass, and wood, paper, printing paper and fiber.

[0067]

Preferred recording media of the present invention are non-absorptive media in which ink is not absorbed into the printing media.

[0068]

<<Ink Colorants>>

Ink colorants employed in the present invention will now be described.

[0069]

When the ink composition according to the present invention is to be colored, colorants are incorporated in the aforesaid ink composition. Employed as colorants may be various types of colorants which are capable of being dissolved in or dispersed into the main component of the polymerizable compound. From the viewpoint of weather resistance, pigments are preferred.

[0070]

Pigments which are preferably employed in the present invention are listed below.

C.I. Pigment Yellow-1, 3, 12, 13, 14, 17, 81, 83, 87, 95, 109, and 42

C.I. Pigment Orange-16, 36, and 38

C.I. Pigment Red-5, 22, 38, 48 : 1, 48 : 2, 48 : 4, 49 : 1, 53 : 1, 57 : 1, 63 : 1, 144, 146, 185, and 101

C.I. Pigment Violet-19 and 23

C.I. Pigment Blue-15 : 1, 15 : 3, 15 : 4, 18, 60, 27, and 29

C.I. Pigment Green-7 and 36

C.I. Pigment White-6, 18, and 21

C.I. Pigment Black-7

Further, in the present invention, in order to enhance covering power of color on transparent substrates such as plastic film, it is preferable to use a white ink. Specifically, in soft package printing and label printing, it is preferable to use a white ink. However, since the ejection amount increases, from the viewpoint of the aforesaid ejection stability, and the formation of curling and wrinkling, the amount to be used is obviously limited. [0071]

The aforesaid pigments may be dispersed employing, for example, a ball mill, a sand mill, an attritor, a roller mill, an agitator, a Henschel mill, a colloid mill, an ultrasonic homogenizer, a pearl mill, a wet type jet mill, and a paint shaker. Further, during dispersion of pigments,

it is possible to add dispersing agents. Preferably employed as dispersing agents are polymer dispersing agents. Listed as polymer dispersing agents are Solsperse Series available from Avecia Co. Further, employed as dispersing aids may be synergists corresponding to each of various types of pigments. The added amount of the aforesaid dispersing agents and dispersing aids is preferably 1 - 50 parts by weight with respect to 100 parts by weight of the pigments. Dispersion media are comprised of solvents or polymerizable compounds. In the radiation curable type ink employed in the present invention, in order to allow the aforesaid ink to undergo reaction and curing, it is preferable to avoid solvents. When solvents remain in cured images, solvent resistance is degraded and VOC problems of remaining solvents also occur. Therefore, it is preferable that in the dispersion media, polymerizable compounds are used instead of solvents. Of polymerizable compounds, from the viewpoint of appropriate dispersion, it is preferable to select monomers at the lowest viscosity.

[0072]

Pigments are preferably dispersed to result in an average particle diameter of 0.08 - 0.5  $\mu\text{m}$ . Suitably pigments, dispersing agents, dispersion media, dispersing



conditions and filtering conditions are selected and set so that the maximum particle diameter is controlled to be in the range of 0.3 - 10  $\mu\text{m}$  and preferably 0.3 - 3  $\mu\text{m}$ . By the aforesaid particle diameter management, it is possible to minimize clogging of head nozzles, as well as to maintain storage stability of the ink, ink transparency and curing speed.

[0073]

The concentration of colorants in the photocurable ink according to the present invention is preferably 1 - 10 percent by weight with respect to the total ink.

[0074]

<<Colorants>>

Colorants employed in the present invention will now be described.

[0075]

Examples of colorants include various colored organic pigments such as phthalocyanine based, azo based, quinacridone based, dioxazine based, and diketopyrrolopyrrole based, as well as inorganic pigments such as carbon black, titanium white, silica, mica, and zinc oxide.

[0076]

The concentration of colorants in the photocurable ink according to the present invention is preferably in the range of 1 - 15 percent by weight of the total ink, and is more preferably in the range of 1 - 10 percent by weight.

[0077]

<<Activators (also called Surface Active Agents)>>

In order to control surface tension, if desired, surface active agents may be incorporated. Examples of surface active agents, which are preferably employed in the present invention, include anionic surface active agents such as dialkylsulfosuccinic acid salts, alkyl naphthalenesulfonic acid salts, and fatty acid salts; nonionic surface active agents such as polyoxyethylene alkyl allyl ethers, acetylene glycols, and polyoxyethylene-polyoxypropylene block polymers; and cationic surface active agents such as alkylamine salts and quaternary ammonium salts. Of these, specifically preferred are anionic surface active agents as well as nonionic surface active agents.

[0078]

<<Solvents>>

If desired, solvents may be incorporated in actinic radiation curable ink-jet ink compositions. It is possible to use actinic radiation curable compositions which are

diluted by, for example, ketones such as methyl ethyl ketone and methyl isobutyl ketone, acetic acid esters such as butyl acetate, aromatic hydrocarbons such as benzene, toluene, and xylene, alcohols such as ethylene glycol monoacetate and propylene glycol dimethyl ether, and water and frequently employed common organic solvents.

[0079]

The concentration of solvents in the photocurable ink according to the present invention is preferably at most 5 percent by weight with respect to the total ink.

[0080]

#### <<Polymerization Inhibitors>>

Examples of preferred polymerization inhibitors employed in the present invention include p-methoxyphenol, hydroquinone, methoxybenzoquinone, phenothiazine, catechols, alkylphenols, alkylbisphenols, zinc dimethyldithiocarbamate, copper dimethylthiocarbamate, copper dibutylthiocarbamate, copper salicylate, thiodipropionic acid esters, mercaptobenzimidazole, and phosphites. Of these, specifically preferred are p-methoxyphenol, catechols, and phenols.

[0081]

Examples of catechols include p-t-butylcatechol.

Further, listed as phenols are 2,6-di-t-butylphenol, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-hydrocinnamide), 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-methylenebis(2,6-di-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)4-methylphenol, 1,1,3-tris(2'-methyl-5'-t-butyl-4'-hydroxyphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3'-5'-di-t-butyl-4'-hydroxybenzyl)benzene, triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], pentaerithrytyltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], and 2-t-butyl-6-(3-t-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate. In the present invention preferred are those which are oil-soluble.

[0082]

(Used Amount of Polymerization Inhibitors)

Polymerization inhibitors may be employed individually or in combinations of at least two types. The added amount of the aforesaid polymerization inhibitors is customarily 100 - 10,000 ppm with respect to the total ink weight, is preferably 300 - 2,000 ppm, and is more preferably 500 - 1,000 ppm.

[0083]

## [DESCRIPTION OF THE PREFERRED EMBODIMENTS]

## &lt;&lt;Recording Apparatus&gt;&gt;

The recording apparatus employed in the present invention will now be described.

[0084]

The recording apparatus employed in the present invention will now be described with reference to a drawing when deemed necessary. Further, the recording apparatus in the drawing is one of the embodiments employed in the present invention, but the recording apparatus employed in the present invention is not limited thereto.

[0085]

Fig. 1 is a front view showing the structure of the main section of the recording apparatus employed in the present invention. Recording apparatus 1 is comprised of head carriage 2, recording head 3, illumination means 4, and platen section 5. Platen section 5 exhibits an ultraviolet radiation absorbing function and absorbs extra ultraviolet radiation which has been transmitted through recording material P. As a result, it is possible to very consistently reproduce highly fine and detailed images.

[0086]

Recording material P is guided by guide member 6 and moves from the front to the back of Fig. 1, utilizing operation of a transport means (not shown). A head scanning means (also not shown) allows head carriage 2 to reciprocate in the Y direction shown in Fig. 1 whereby scanning of recording head 3, held by head carriage 2, is carried out.

[0087]

Head carriage 2 is arranged above recording material P, and houses a plurality of recording heads 3, described below, matching the number of colors employed for printing images onto recording material P so that ink ejection openings are arranged on the lower side. Head carriage 2 is arranged in the main body of recording apparatus 1 in such manner that reciprocal motion is allowed in the Y direction in Fig. 1. driven by the head scanning means.

[0088]

Incidentally, Fig. 1 shows that head carriage 2 houses yellow (Y), magenta (M), cyan (C), and black (K) recording heads 3. However, in practice, the number of colors of recording head 3, which are housed in carriage 2, is decided on a need basis.

[0089]

Recording heads 3 eject a photocurable ink (also called an actinic radiation curable ink such as an ultraviolet radiation curable ink), which is supplied by an ink supply means (not shown), onto recording material P from ejection openings, utilizing operation of a plurality of ejection means (also not shown) arranged in its interior. The ultraviolet radiation curable ink (also called UV ink), which is ejected from recording heads 3, is comprised of colorants, polymerizable monomers, initiators, and the like. When exposed to ultraviolet radiation, the aforesaid initiators work as a catalyst, whereby curing properties are exhibited through crosslinking and polymerization reaction of the aforesaid monomers.

[0090]

During scanning in which recording heads 3 move from one end of recording material P to the other end thereof along the Y direction in Fig. 1, while driven by the head scanning means, aforesaid recording heads 3 eject the aforesaid UV ink in the form of ink droplets onto a definite region (an ink droplet receivable area) of recording material P and impinge ink droplets onto the aforesaid ink droplet receivable area.

[0091]

The aforesaid scanning is carried out at a suitable frequency. The aforesaid UV ink is ejected onto the ink droplet receivable region. Thereafter, recording material P is appropriately conveyed from the front to the back of Fig. 1, employing a conveying means, and scanning is again carried out employing the head scanning means. During the aforesaid scanning, the aforesaid UV ink is ejected onto the following ink droplet receivable region adjacent to the backward direction of Fig. 1, while employing recording heads 3.

[0092]

The aforesaid operation is then repeated. By ejecting the aforesaid UV ink from recording heads 3 while synchronizing the head scanning means with the conveying means, an image comprised of an assembly of UV ink droplets is formed on recording material P.

[0093]

Exposure means 4 is comprised of an ultraviolet radiation lamp which emits ultraviolet radiation of a specified wavelength region at consistent exposure energy, and a filter which transmits the ultraviolet radiation of the specified wavelength. Herein, employed as ultraviolet radiation lamps may be mercury lamps, metal halide lamps, excimer lasers, ultraviolet lasers, cold cathode tubes,



black-light lamps, and LEDs (light emitting diodes). Of these, preferred are band-shaped metal halide lamp tubes, cold cathode tubes, mercury lamps, or black-light lamps. Specifically, preferred are cold cathode tubes and black-light lamps which emit ultraviolet radiation of a wavelength of 365 nm, because bleeding is minimized, dot diameter is efficiently controlled, and wrinkling during curing is minimized. By employing the black light lamp as a radiation source of exposure means 4, it is possible to prepare exposure means 4 to cure the UV ink at a lower cost.

[0094]

Exposure means 4 is shaped to be nearly equal to the maximum one which can be set by recording apparatus (being a UV ink-jet printer) 1 of the ink dot receivable region in which the UV ink is ejected during one frequency of scanning in which recording heads 3 are driven by the head scanning means, or is shaped to be larger than the ink dot receiving region.

[0095]

Exposure means 4 are arranged and fixed on both sides of head carriage 2, being nearly parallel to recording material P.

[0096]

As noted above, as a means to control illuminance in the ink ejection section, needless to say, entire recording heads 3 are shielded from light. In addition, it is effective that distance  $h_2$  between ink ejection section 31 of recording heads 3 and recording material P is adjusted to be greater than distance  $h_1$  between exposure means 4 and recording material P (i.e.,  $h_1 < h_2$ ) and/or distance  $d$  between recording heads 3 and exposure means 4 increases ( $d$  increases). Further, it is more preferable that bellows structure 7 is applied between recording heads 3 and exposure means 4.

[0097]

Herein, it is possible to suitably change the wavelength of ultraviolet radiation which is exposed employing exposure means 4 by replacing ultraviolet radiation lamps or filters fitted with exposure means 4.

[0098]

Other than common coated paper and non-coated paper, employed as recording materials may be various types of non-absorptive plastics and film thereof which are employed in so-called soft packaging. Examples of various types of plastic film include PET (polyethylene terephthalate) film, OPS (oriented polystyrene) film, OPP (oriented polypropylene)

film, ONy (oriented nylon) film, PVC (polyvinyl chloride) film, PE film, and TAC film. Employed as other plastic film may be polycarbonate, acrylic resins, ABS, acetal, PVA, and rubber. Further, metal and glass may also be employed.

[0099]

Of these recording materials, when images are formed specifically on PET film, OPS film, OPP film, ONy film, or PVC film which are thermally shrinkable, the effects of the present invention are more pronounced. These substrates tend to curl and deform due to contraction during ink curing and heat generated during the curing reaction. In addition, it is difficult for the ink layer to keep up with contraction of the aforesaid substrate.

[0100]

In the present invention, from the viewpoint of the cost of recording materials such as packaging cost as well as production cost, print production efficiency, and compatibility with prints of various sizes, it is more advantageous to use long (web) recording materials.

[0101]

<<Exposure Apparatus and Types of Light (electromagnetic radiation) Employed for Light Exposure>>

Photocurable ink according to the present invention is cured when exposed to light. Preferably employed as the aforesaid light (also called electromagnetic radiation) are near infrared radiation, visible light, ultraviolet radiation, and electron beams. Of these, the ultraviolet radiation is most preferably employed.

[0102]

Preferably employed as exposure light sources which emit ultraviolet radiation during exposure, i.e., which emit radiation having wavelengths in the ultraviolet region, are exposure light sources having a peak wavelength (also called dominant wavelength) of 300 - 400 nm. Of these, specifically preferred are those which emit ultraviolet radiation at a peak wavelength of 200 - 420 nm.

[0103]

Examples of exposure light sources include low and high pressure mercury lamps, metal halide lamps, excimer lamps, xenon lamps, halogen lamps, fluorescent lamps, electrode-free UV lamps, lasers, and LEDs.

[0104]

(Input Energy Amount to Exposure Light Source)

Exposure means employed for light exposure according to the present invention may be arranged parallel to the nozzle

arrangement of the head of the recording apparatus shown in Fig. 1, or in the direction across the width of the substrate. In the invention described in claim 1, in order to achieve the effects described in the present invention, essential conditions are that the input energy amount to the light source for the aforesaid exposure is 0.1 - 50 W/cm, and is preferably 0.1 - 20 W/cm. Further, the distance from the substrate to the light emitting surface of the light source is preferably 0.1 mm - 20 cm.

[0105]

In the present invention, when the energy input amount to the light source employed for light exposure is less than 0.1 W/cm, photocurable ink compositions are not sufficiently cured. On the other hand, when the aforesaid input energy amount exceeds 50 W/cm, problems such as cracking tend to result due to curing contraction on the ink surface formed on a recording medium after impingement of the photocurable ink.

[0106]

Herein, it is possible to adjust the aforesaid input energy amount by controlling voltage and electric current, using conventional constant-voltage power supplies, known in the art. It is possible to measure the aforesaid input

energy amount employing, for example, UIT-150 (manufactured by Ushio Denki Co.).

[0107]

(Time between Ink Impingement and Light Exposure)

The preferred light exposure method in the present invention is that a light source is arranged across the printing width and ultraviolet radiation is applied a definite period of time after ink impingement.

[0108]

In the image forming method described in claim 2 of the present invention, from the viewpoint of minimizing head staining due to sublimated materials formed by curing, as well as minimizing nozzle clogging due to stray light, and minimizing degradation of image quality due to fluctuation of the dot shape caused by variations of the substrate, light exposure is carried out 0.001 - 2 seconds after ink impingement and is more preferably 0.01 - 1 second.

[0109]

(Measurement of Time between Ink Impingement and Light Exposure)

In the case of an exposure method having a gradient of illuminance in the exposed area, the time between the ink impingement and the exposure is measured in such manner that

when illuminance reaches at least 1/10 of the maximum illuminance, the resulting time is regarded as the exposure initiating time.

[0110]

[EXAMPLES]

The present invention will now be specifically described with referenced to examples. However, the present invention is not limited thereto.

[0111]

Example 1

<<Preparation of Ink Composition>>

Tables 1 - 4 show Ink Composition Sets (also simply called Ink Sets) 1 - 4, while Table 5 shows Comparative Ink Composition Set 5. Further, each of the numerical figures shown in Tables 1 - 5 refer to parts by weight in the ink compositions.

[0112]

Incidentally, ink was prepared employing methods commonly known in the art of this industry.

[0113]

(Table 1)

Ink Composition Set 1		K	C	M	Y
Colorant (% by weight)		Colorant 1 2.5	Colorant 2 2.5	Colorant 3 2.5	Colorant 4 2.5
Position 2 Substituted Oxetane Compound	2-methoxy-3,3-dimethyl-oxetane	100	100	100	100
OXT221 (Comparative Oxetane)		-	-	-	-
Celoxide 2021P (Photo-polymerizable Compound)		-	-	-	-
CI-5102		5	5	5	5
CS-7102		1	1	1	1



[0114]

(Table 2)

Ink Composition Set 2		K	C	M	Y
Colorant (% by weight)		Colorant 1 2.5	Colorant 2 2.5	Colorant 3 2.5	Colorant 4 2.5
Position 2 Substituted Oxetane Compound	2-methoxy-3,3-dimethyl-oxetane	30	30	30	30
OXT221 (Comparative Oxetane)		40	40	40	40
Celoxide 2021P (Photo-polymerizable Compound)		30	30	30	30
CI-5102		5	5	5	5
CS-7102		1	1	1	1

[0115]

(Table 3)

Ink Composition Set 3		K	C	M	Y
Colorant (% by weight)		Colorant 1 2.5	Colorant 2 2.5	Colorant 3 2.5	Colorant 4 2.5
Position 2 Substituted Oxetane Compound	2,2,3,3-tetramethyl-oxetane	100	100	100	100
OXT221 (Comparative Oxetane)		-	-	-	-
Celoxide 2021P (Photo-polymerizable Compound)		-	-	-	-
CI-5102		5	5	5	5
CS-7102		1	1	1	1

[0116]

(Table 4)

Ink Composition Set 4		K	C	M	Y
Colorant (% by weight)		Colorant 1 2.5	Colorant 2 2.5	Colorant 3 2.5	Colorant 4 2.5
Position 2 Substituted Oxetane Compound	2-methoxy-3,3-dimethyl-oxetane	50	50	50	50
OXT221 (Comparative Oxetane)		50	50	50	50
Celoxide 2021P (Photo-polymerizable Compound)		-	-	-	-
CI-5102		5	5	5	5
CS-7102		1	1	1	1

[0117]

(Table 5)

Ink Composition Set 5 (Comparative)	K	C	M	Y
Colorant (% by weight)	Colorant 1 2.5	Colorant 2 2.5	Colorant 3 2.5	Colorant 4 2.5
Position 2 Substituted Oxetane Compound	-	-	-	-
OXT221 (Comparative Oxetane)	70	70	70	70
Celoxide 2021P (Photopolymerizable Compound)	-	-	-	-
CI-5102	5	5	5	5
CS-7102	1	1	1	1

[0118]

Each of the compounds described in Tables 1 - 5 is detailed below.

K: concentrated black ink

C: concentrated cyan ink

M: concentrated magenta ink

Y: concentrated yellow ink

Colorant 1: C.I. Pigment Black-7

Colorant 2: C.I. Pigment Blue-15 : 3

Colorant 3: C.I. Pigment Red-57 : 1

Colorant 4: C.I. Pigment Yellow-13

Photopolymerizable Compound: Celoxide 2021P, manufactured by Daiseru Kagaku Kogyo Co.

Oxetane Compound: OXT221, manufactured by Toa Gosei Kagaku Co.

CI-5102: a product manufactured by Nihon Soda Co.

CS-7102: anthracene derivative, manufactured by Nihon Soda Co.

Each of Ink Composition Sets, prepared as above, was loaded in the ink-jet recording apparatus, shown in Fig. 1, which was fitted with piezo type ink nozzles. Each image recording, described below, was continuously carried out on each of 600 mm wide 1,000 m long recording materials. The

ink supply system was comprised of an ink tank, a supply pipe, a pre-chamber ink tank immediately prior to the head, piping fitted with filters, and a piezoelectric head. The aforesaid ink supply system was heated to 50 °C, while the system from the pre-chamber tank to the head portion was insulated from heat. The aforesaid piezo head was driven to eject multi-size dots of 2 - 15 pl at a resolution of 720 dpi x 720 dpi (dpi refers to the number of dots per inch or per 2.54 cm) and each ink was continuously ejected. Curing was conducted out 0.2 second after ink impingement at exposure timing (light exposure conditions) described in Table 6, whereby Ink-jet Image Recorded Samples (also simply called Samples) 1 - 6 were prepared.

[0119]

Further, in the recording apparatus described in Table 1, it is possible to regulate the amount of light exposure energy onto the ink surface by varying the distance between the head and the exposure light source as well as the conveying rate of the media.

[0120]

<<Evaluation of Ink-jet Image Recorded Samples 1 - 6>>

Ink-jet Image Recorded Samples 1 - 6 were subjected to evaluation of scratch resistance as well as adhesion properties, as described below.

[0121]

<<Evaluation of Scratch Resistance>>

The surface of each solid image patch was scanned employing a Scratch Resistance Tester (HEIDON-18, manufactured by HEIDON Co.). Scanning was carried out employing a 1.00 mmR sapphire needle while varying the load from 0 to 200 g. The lowest weight which resulted in scratches was determined and the average value of four colors (K, M, Y, and C) was determined.

[0122]

<<Evaluation of Adhesion Property>>

The surface of a solid printed image was subjected to cutting of 6 longitudinal lines and 6 lateral lines, employing a razor so that cutting depth did not reach the recording medium, whereby 25 squares were formed. Subsequently, 25 mm wide Cellotape Tape (registered trade mark) or cellophane tape was adhered onto the resulting squares and sufficiently pressed. Thereafter, the cellophane tape was rapidly peeled at a peeling angle of 90 degrees and the number of squares which exhibited peeling was determined.

Evaluation was ranked as A - E, and carried out based on the criteria described below.

[0123]

In the following ranks, A and B were judged to be commercially viable.

A: No square exhibited peeling

B: 1 - 3 squares exhibited peeling

C: 4 - 10 squares exhibited peeling

D: 11 - 25 squares exhibited peeling

E: At least 26 squares exhibited peeling

Table 6 shows the evaluation results.

[0124]

(Table 6)

Ink-jet Image Recorded Sample No.	Ink Set	Exposure Apparatus	Input Power W/cm	Scratch Resistance	Adhesion Property	Re- marks
1	1	black-light	0.4	120	A	Inv.
2	2	black-light	0.4	150	A	Inv.
3	3	black-light	0.4	130	A	Inv.
4	4	black-light	0.4	130	A	Inv.
5	5	black-light	0.4	50	B	Comp.
6	1	high pressure mercury	100	50	C	Comp.

Inv.; Present Invention

Comp.; Comparative Example

[0125]

As can clearly be seen from Table 6, Samples 1 - 4 in which ink-jet images were formed employing the ink comprising a compound having an oxetane ring in which at least position 2 was substituted while the input energy amount to the light source used for exposure was maintained in the range of 0.1 - 50 W/cm, exhibited high scratch resistance of the resulting ink surface (also called an ink-jet image surface) and excellent adhesion property, compared to Samples 5 and 6 which were not prepared as above.

[0126]

#### Example 2

Ink Composition Sets 1 - 5 were prepared in the same manner as Example 1. Subsequently, ink-jet images were formed in the same manner as Example 1, except that exposure timing was varied as described in Table 7, while setting the light exposure amount at 10 mJ/cm<sup>2</sup>. Resulting Ink-jet Image Recorded Samples 7 - 13 were subjected to each of the evaluation described below.

[0127]

The light exposure amount was determined employing UV40D/V (manufactured by Ushio Denki Co.).

<<Character Quality>>



At the target density of each of colors Y, M, C, and K, 6-point MS Ming-style characters were printed and jaggedness of characters was evaluated employing a common magnifying glass.

[0128]

A: No jaggedness was noticed

B: Slight jaggedness was noticed

C: Jaggedness was noticed but characters were identifiable, resulting in the lower limit for commercial viability

D: Jaggedness was pronounced, resulting in no commercial viability due to blurring of characters

<<Color Mixing (Bleeding)>>

Dots of each color, adjacent to each other, were visually evaluated employing a common magnifying glass.

[0129]

A: The shapes of dots adjacent to each other were circular, resulting in no bleeding

B: The shapes of dots adjacent to each other were nearly circular, exhibiting almost no bleeding

C: Dots adjacent to each other exhibited slight bleeding and the dot shapes were slightly deformed, resulting in the lower limit for commercial viability

D: Dots adjacent to each other exhibited bleeding and mixing,

resulting in a commercially unviable product

Table 7 shows the results.

[0130]

(Table 7)

Ink-jet Image Recorded Sample No.	Ink Set	Exposure Apparatus	Exposure Timing	Character Quality	Bleeding	Remarks
7	1	black-light	0.4 second	A	A	Inv.
8	2	black-light	0.4 second	A	A	Inv.
9	3	black-light	0.4 second	A	A	Inv.
10	4	black-light	0.4 second	A	A	Inv.
11	1	high pressure mercury	0.4 second	B	B	Inv.
12	5	black-light	0.4 second	C	D	Comp.
13	1	black-light	3 seconds	D	D	Comp.

Inv.; Present Invention

Comp.; Comparative Example

[0131]

As can clearly be seen from Table 7, Samples 7 - 11 in which exposure initiation time, after the aforesaid photocurable ink ejected from the ink-jet head was impinged on the substrate, was maintained in the range of 0.001 - 2 seconds and ink comprising an oxetane compound, in which at

least position 2 was substituted was employed, exhibited excellent character quality, and resulted in no color mixing, compared to Samples 12 and 13 which were not prepared as above.

[0132]

#### Example 3

Ink Composition Sets 1 - 5 were prepared in the same manner as Example 1. Subsequently, ink-jet images were formed in the same manner as Example 1, except that illuminance ( $\text{mW}/\text{cm}^2$ ) on the substrate surface after ink ejection (also called ink discharge) was varied as shown in Table 8. Resulting Ink-jet Image Recorded Samples 14 - 19 were evaluated in the same manner as Example 1.

[0133]

Illuminance during light exposure was determined employing UV40D/V (manufactured by Ushio Denki Co.). Table 8 shows the results.

[0134]

(Table 8)

Ink-jet Image Recorded Sample No.	Ink Set	Exposure Apparatus	Illumi- nance mW/cm <sup>2</sup>	Exposure Light Amount mJ/cm <sup>2</sup>	Scratch Resist- ance	Adhe- sion Prop- erty	Re- marks
14	1	black- light	5	3	120	A	Inv.
15	2	black- light	5	5	150	A	Inv.
16	3	black- light	5	3	130	A	Inv.
17	4	black- light	5	3	130	A	Inv.
18	5	black- light	5	15	50	B	Comp.
19	1	high pressure mercury	100	3	50	C	Comp.

Inv.; Present Invention

Comp.; Comparative Example

[0135]

As can clearly be seen from Table 8, Samples 14 - 17 in which ink-jet images were formed, while illuminance on the substrate surface during light exposure was controlled to be in the range of 0.1 - 50 mW/cm at 200 - 450 nm, while regulating the energy input amount to the light source and ink was used which comprised compounds having oxetane ring(s) in which at least position 2 was substituted, exhibited high scratch resistance of the resulting ink surface (also called

the ink-jet image surface) as well as excellent adhesion property, compared to Samples 18 and 19 which were not prepared as above.

[0136]

[EFFECTS OF THE INVENTION]

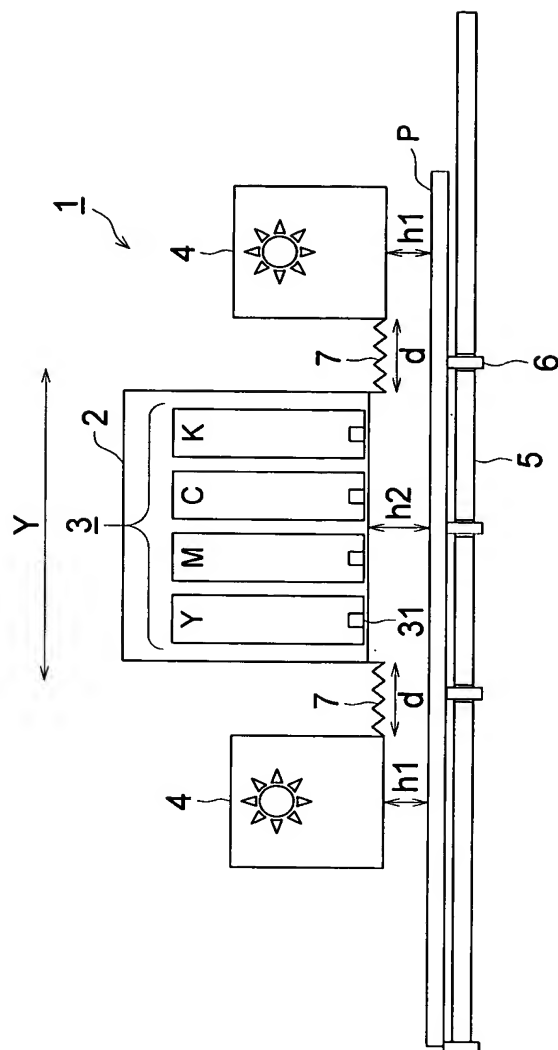
According to the present invention, it is possible to provide an ink-jet image forming method which exhibits a high speed, high scratch resistance, and excellent adhesion property.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a front view showing the structure of the main section of the recording apparatus employed in the present invention.

[DESCRIPTION OF NUMBERED AND SYMBOLIZED ITEMS]

- 1 recording apparatus
- 2 head carriage
- 3 recording heads
- 4 exposure means
- 5 platen section
- 6 guide member
- 7 bellows structure
- P recording material



[NAME OF DOCUMENT]

ABSTRACT

[SUMMARY]

[PROBLEMS TO BE SOLVED] To provide an ink-jet image forming method which exhibits a high speed, high scratch resistance, and excellent adhesion property.

[MEANS TO SOLVE THE PROBLEMS] In an image forming method in which a photocurable ink is ejected onto a substrate employing an ink-jet head and subsequently light exposure is carried out to form an image, an ink-jet image forming method characterized in that the energy input amount to an exposure light source employed for the aforesaid light exposure is 0.1 - 50 W/cm and the aforesaid photocurable ink comprises compounds having oxetane ring(s) in which at least position 2 is substituted.

[SELECTED DRAWINGS]      None